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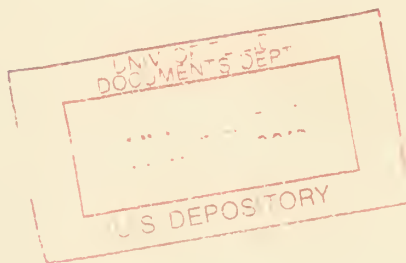
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CONDENSED WATER IN WOOD**

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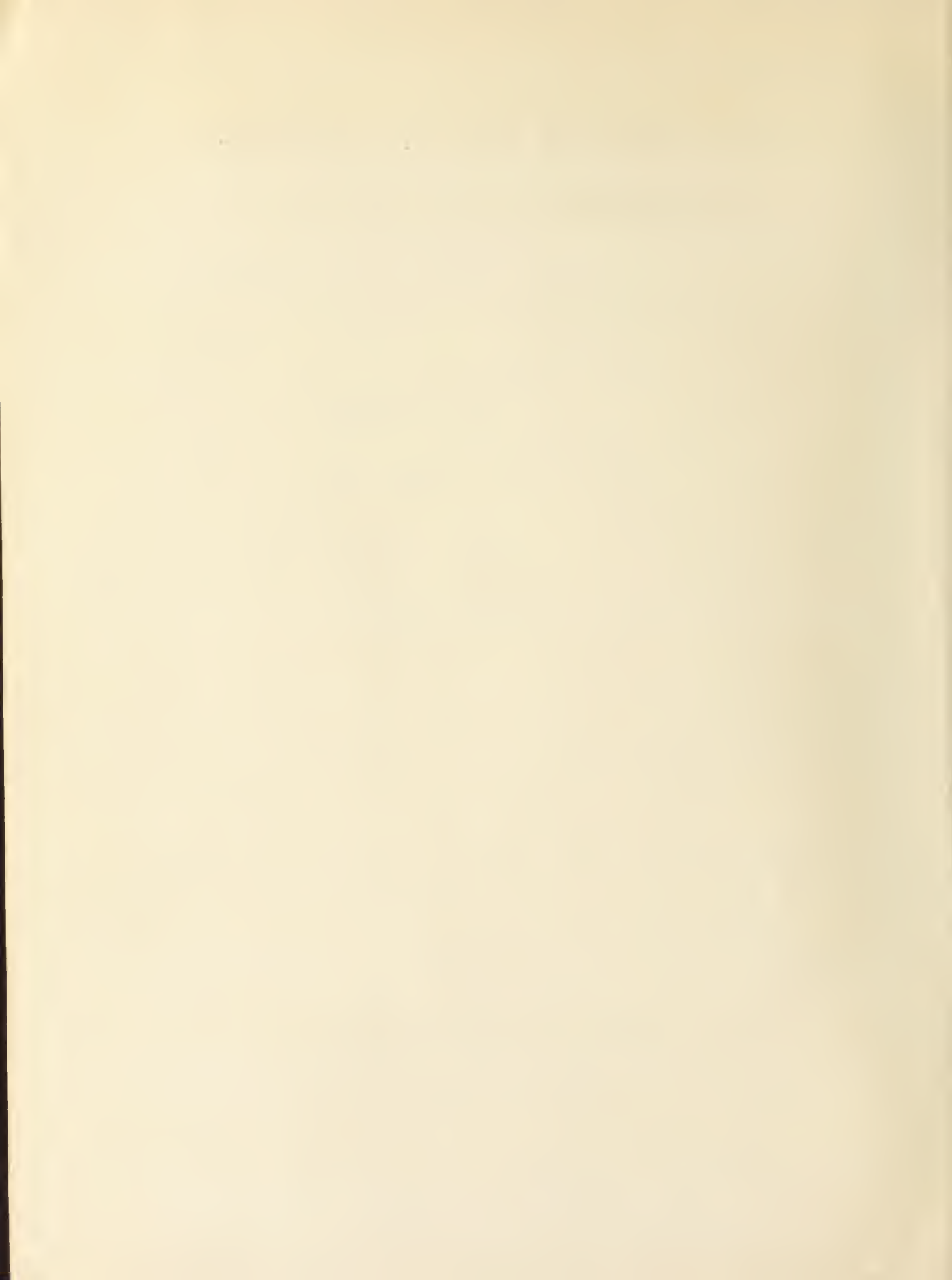
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**UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison, Wisconsin**

In Cooperation with the University of Wisconsin



SURFACE-BOUND VERSUS CAPILLARY-CONDENSED WATER IN WOOD¹

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It is generally conceded that the water held by cellulose and by wood with a reduction in the equilibrium relative vapor pressure is held either by direct surface molecular forces or by capillary condensation. The extent to which each of these is effective is, however, still controversial. Sheppard and Newsome (6) and Stamm (3) have taken the stand that the inflection point in the sigmoid moisture content-relative vapor pressure curves roughly represents the transition point between surface-bound and capillary-held water, the curve being a combination of an adsorption curve, which tends to become parallel to the relative vapor pressure axis, and a capillary condensation curve, which becomes effective in capillaries just slightly exceeding molecular dimensions and tends to become parallel to the moisture content axis. On this basis the surface-bound water would vary from 3 to 7 percent for different celluloses and wood, and the capillary-condensed water would amount to 12 to 25 percent.

Other evidence that the surface-bound water is of this order of magnitude is obtained from the thermodynamic calculations of Stamm and Loughborough (10). The temperature coefficient of the differential heat of swelling-moisture content relationship becomes significant above this moisture content. Presumably the temperature coefficient of capillary condensation is appreciably greater than that of surface adsorption. The entropy change-moisture content relationship further has an inflection point around 6 percent moisture content, indicating a change in the energy relationship. Extrapolation of the relationship between moisture sorption and temperature at saturated vapor pressures to the critical temperature should give a strictly surface adsorption value. Although this extrapolation cannot be made with any degree of accuracy, available data (10) indicate that the surface-bound water on this basis cannot exceed a few percent. Predicted values of the surface-bound water of 20 percent (2) are quite incompatible with these data, as the sorption only slightly exceeds 20 per cent at the experimental temperature of 100° C.

A number of investigators have differentiated between surface-bound water, capillary-held water, and free water on the basis of the first not acting as a solvent for solutes (5). From studies of the effect of salts

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(7) and sugars (9) upon the shrinking of wood, Stamm concluded that practically all the sorbed water would act as a solvent. These solutes reduced the shrinkage of wood to the oven-dry condition by an amount which would be obtained if the treating solution attained a concentration within the swelling structure practically equal to the bulk concentration and the solute were subsequently deposited within this structure on drying. The accuracy of these measurements is such as to indicate that selective adsorption of water cannot exceed a few percent.

Barkas (1, 2) has made measurements of the selective adsorption from sugar solutions by wood, from which the air was removed by a special vacuum device to avoid all capillary effects, using an interferometer method to determine the concentration changes. From these data he calculated a minimum value for the bound water for each concentration by considering that sugar is not adsorbed.² He concluded that approximately 20 percent of water does not act as a solvent. This value is about three times the estimated value of the surface-bound water from the relative vapor pressure-moisture content curves and the thermal data and is incompatible with measurements of the retardation of shrinkage caused by solutes deposited in the cell wall. It thus seemed desirable to repeat Barkas' measurements with sugar and also to make them with other solutes.

Adsorption Measurements

The measurements of the selective adsorption of water from aqueous solutions by wood were made with a Hilger-Raleigh gas cell interferometer adapted for use as a liquid cell interferometer in a manner somewhat similar to that used by Ford and McBain (3) and Hall and Jones (4). A water bath was built into the tube zone of the instrument with plate glass windows at the two ends set in adjustable rubber diaphragms. This made possible the perfect alignment of the fringes when the bath was full of water. The cells were made by sealing a piece of 10-mm. Pyrex tubing concentrically into a piece of 40-mm. tubing with an inner seal connection serving for filling (4). Ground Pyrex glass plates were sealed to the parallel ground ends of tubes with silver chloride cement. The cells used ranged from 7 to 12 cm. in length. This simple construction makes it readily possible to set the cell in such a position that the two beams which give fixed reference fringes and the comparison beam all pass through the solution of lowest refractive index in the large outer tube part of the cell and the adjustable fringe beam passes through the solution of higher index of refraction in the inner tube part of the cell. In all cases investigated the fringe displacement was found to be directly proportional to the concentration.

²What seems to be a typographical error occurs in the derivation of Barkas' equation. The final form of the equation and the calculations made therefrom, however, are correct.

Sugar pine, in the form of small thin sections about 1 mm. in the fiber direction, was used for the measurements. To insure the removal of all extractives the sections were extracted in a continuous extractor with each of the following solvents for 7 days: benzene, methyl alcohol, and water. They were then oven-dried prior to use. Chemically pure sucrose (in the form of rock candy), glycerol, and sodium chloride were used as the solutes. Precautions were taken in the case of the sucrose to perform all operations under sterile conditions. For each measurement 0.3 to 2.5 g. of oven-dry wood was used and enough solution to give ratios of the weight of solution to that of the wood of 20 to 200. A vacuum device, very similar to that of Barkas (2), was used for removing the air from the thin wood sections and for running the solution of known concentration on the wood without loss of solvent. The solutions were allowed to stand in contact with the wood for a minimum time of 24 hours at 25° C., after which the equilibrium concentration of the solution was determined with the interferometer, using the original solution as the reference solution.

In the three different solutions used in this investigation, selective adsorption of water took place. Preliminary measurements with other solutions indicate that water is selectively adsorbed from all aqueous solutions that cause a negligible swelling of the wood beyond the water-swollen dimensions, whereas the solute is selectively adsorbed from aqueous solutions that cause an appreciable swelling of the wood beyond water swollen dimensions. The calculations of the minimum amount of selectively adsorbed water were made by assuming that the adsorption of solute was negligible (2). On this basis the weight of the adsorbed water per gram of dry wood that does not act as a solvent is given by the following equation:

$$w_a = \frac{M}{X} \left(\frac{\Delta C}{C_2} \right) \quad (1)$$

in which M is the weight of solution in grams in contact with X grams of dry wood, ΔC is the concentration change, and C_2 the equilibrium concentration in grams of solute per gram of solution.

In figure 1 the percentage by weight of water held by the wood that does not act as a solvent is plotted against the concentration of the solution in equilibrium with the wood in weight percent. The data for the sugar solutions are very scattered, but are in fairly good agreement with the data of Barkas except at low concentrations.

The different solutions, on a weight concentration basis, give different values for w_a . This would be expected, as the capacity of the wood to take water from the different solutions should depend upon the activity of the water in these solutions rather than their concentration. This activity is measured by the relative vapor pressure of water over the solutions. In curve B of figure 2 the percentage of water in the wood not acting as a solvent is plotted against the relative vapor pressure of the solution in equilibrium with the wood. In this case all the data

can be reasonably well represented by a single curve which seems to be approaching a limiting value of w_a between 3 and 4 percent; that is, 3 to 4 percent of water is held by the wood without acting as a solvent when in equilibrium with solutions that depress the equilibrium relative vapor pressure by at least 25 percent.

Discussion

If the adsorption of water from solution were strictly a monomolecular surface adsorption of a single constituent on a fixed surface, the adsorption would follow a curve, such as curve C of figure 2. The experimental variation from this curve might be explained in several different ways:

1. The swelling of the wood may increase the internal surface available for water as adsorption continues. Such an increase in surface, however, should give a curve similar to curve C except that it does not become parallel to the relative vapor pressure axis.

2. The solute may be simultaneously adsorbed with the solvent. This would tend to raise curve B and make it more like curve A than curve C.

3. The force of primary adsorption may extend beyond molecular dimensions, causing polymolecular adsorption at high relative vapor pressures. All recent experimental evidence on innumerable systems, however, indicates that polymolecular adsorption does not take place.

4. Capillary condensation may not have been completely eliminated, even though the greatest precautions were taken to do so.

5. Complete equilibrium in the distribution of solvent and solute may not have been attained. It has been demonstrated that water is adsorbed from aqueous solutions by wood, followed by diffusion of the solute into the water within the fine structure (7). The amount of water that can be taken from the solution in this manner will be some function of the relative vapor pressure of the solution. Greater deviations from the true equilibrium condition may thus exist in the least concentrated solutions.

The last two explanations both account for the general nature of curve B. Further experimentation will be necessary, however, to prove that either or both are effective. The data nevertheless show that measurements like those of Barkas (2) in concentrations that do not appreciably depress the relative vapor pressure do not measure the true surface-bound water, and that only in solutions that depress the relative vapor pressure more than 25 percent can approximations of the surface-bound water be made. Innumerable other investigations in which the "bound water" has been obtained by determining the nonsolvent water or water that does not freeze

at an arbitrary temperature are subject to the same error of neglecting the activity of the water. This would be especially true in the case of water-insoluble capillary-active materials in which capillary effects would be most appreciable.

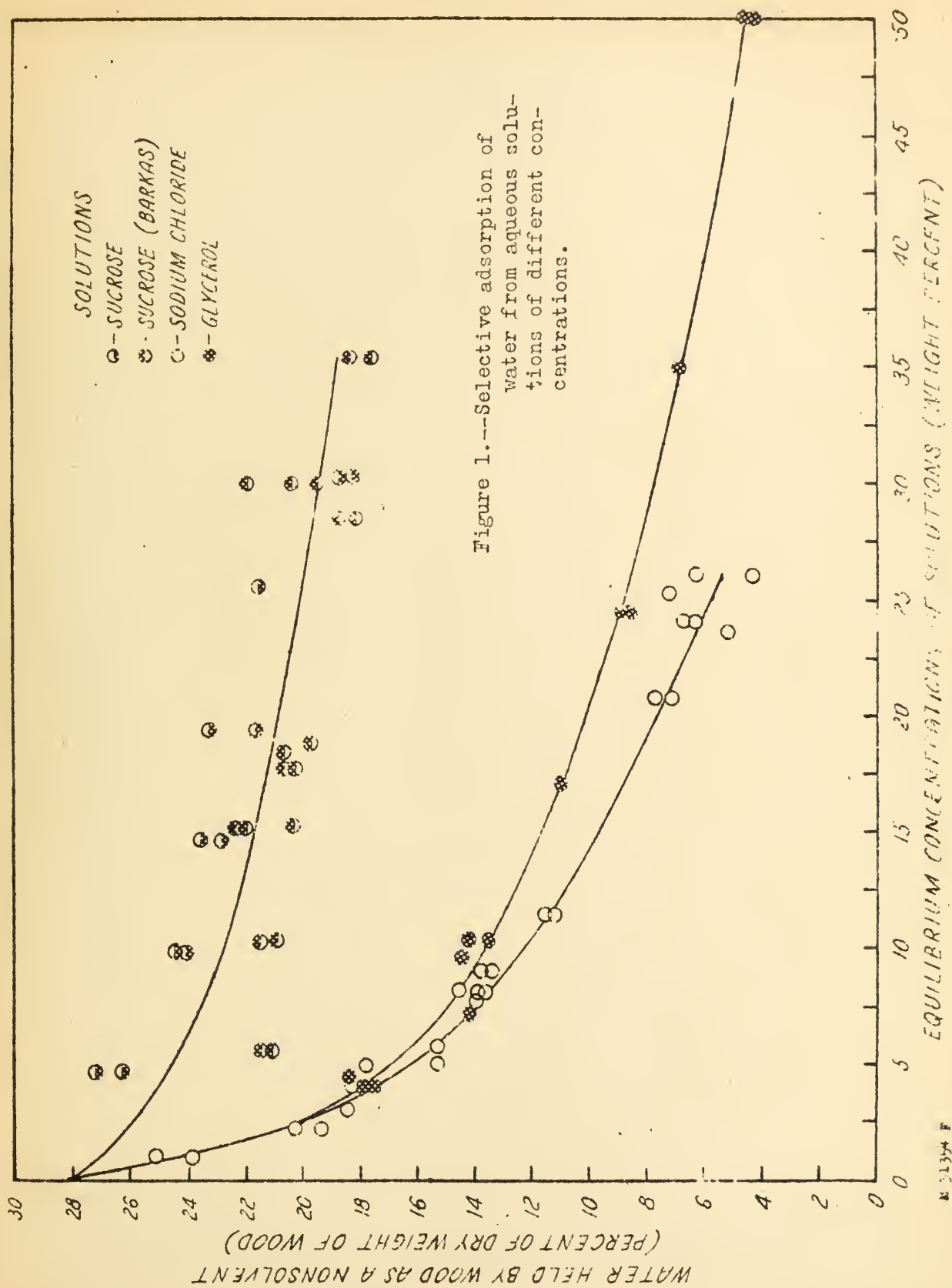
The adsorption of water from solution by the wood, if extended to solutions in equilibrium with 0 percent relative vapor pressure, should follow approximately the dashed part of curve B, figure 2. At relative vapor pressures below 20 to 30 percent the solution should begin to remove surface-bound water from the wood. Curve B falls below curve A in the low relative vapor pressure range, presumably because the surface-bound water shares its bonds between the wood and the adjacent solute molecules. If half of the bonds were shared in this manner, the surface-bound water would be twice the nonsolvent water. In such a case the data would be in excellent agreement with the predictions.

Summary

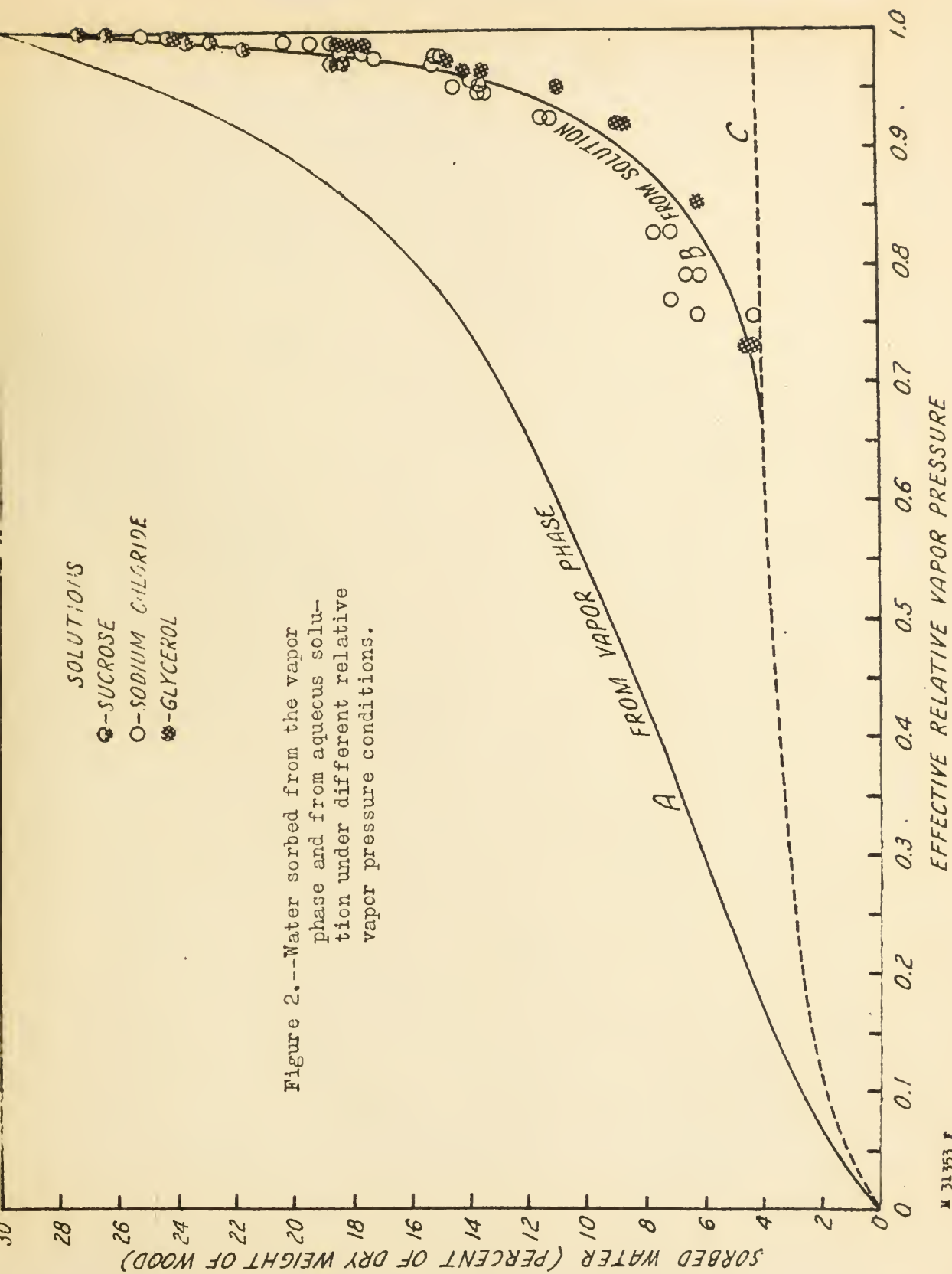
Adsorption measurements from aqueous solutions of sucrose, glycerol, and sodium chloride by wood all give selective adsorption of water. In none of these solutions is wood swollen beyond the water-swollen dimensions. Preliminary measurements of adsorption from solutions causing swelling beyond the water-swollen dimensions indicate that positive adsorption of solute is taking place. The selective adsorption of water from aqueous solutions is a function of the activity of the water in the solution. A constant value of 3 percent is approached in equilibrium with reductions in the relative vapor pressure exceeding 25 percent, which presumably is the adsorption value free from residual capillary condensation and non-equilibrium effects. This value is about half of the predicted surface-bound water. The difference between the values is explained on the basis of the surface-bound water acting as a partial solvent, sharing its bonds between the wood and adjacent solute molecules.

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